

REMARKS

In view of the above amendments and following remarks, reconsideration and further examination are requested.

The specification and abstract have been reviewed and revised to make editorial changes thereto and generally improve the form thereof, and a substitute specification and abstract are provided. No new matter has been added by the substitute specification and abstract.

New formal drawings are provided for Figures 1, 5 and 14 to make these figures more consistent with the written description of the invention. In this regard, in Figure 1, the lead line from "41" is now shown to extend to an electrode within chamber "7". In Figure 5, reference numeral --36a-- has been provided to designate the first connecting member. And, in Figure 14, reference numeral --102-- has been provided, reference numeral "115" to the right of reference numeral "114" has been deleted, and reference numeral "100" at the top of this figure has been changed to reference numeral --101--.

The instant invention pertains to a hydrothermal electrolytic apparatus and a method of using this apparatus. In accordance with a first embodiment of the invention, reference is made to Figures 1-4. In this embodiment, the apparatus comprises a reaction cell for electrolyzing an influent containing water and reducible substances at a temperature of from 100°C to a critical temperature of the influent and at a pressure that allows the water of the influent to be maintained in a liquid phase. The reaction cell includes at least two tubular reaction cells 31 each having a metal inner wall 31a that serves as a cathode, and an anode 41 in each of the at least two tubular reaction cells. The arrangement of a cylindrical metal inner wall as a cathode and an anode surrounded by this metal wall, allows for a surface area of these electrodes to be increased relative to known hydrothermal electrolytic apparatus such that a large amount of influent can be continuously and efficiently electrolyzed. Claims 35 and 47 are believed to be representative of this embodiment of the invention.

In accordance with a second embodiment of the invention, reference is made to Figures 5-9. In this embodiment, like in the first embodiment, the hydrothermal electrolytic apparatus comprises a reaction cell that is for electrolyzing an influent containing water and reducible substances at a temperature of from 100°C to a critical temperature of the influent and at a pressure that allows the

water of the influent to be maintained in a liquid phase. In this embodiment, the reaction cell includes a first electrode having concentrically arranged cylindrical first side walls 37a and a first connecting member 36a that interconnects the first side walls, and a second electrode having concentrically arranged cylindrical second side walls 37b and a second connecting member 36b that interconnects the second side walls. The first side walls 37a and the second side walls 37b are alternately arranged so as to form a channel therebetween for passage of the influent. As with the first embodiment, the arrangement of the first and second electrodes in this embodiment allows for a surface area of these electrodes to be increased relative to surface area of electrodes of a conventional hydrothermal electrolytic apparatus such that a large amount of influent can be continuously and efficiently electrolyzed. Claims 41 and 52 are believed to be representative of this embodiment of the invention.

Additionally, to further increase the surface area of the electrodes, with regard to either of the embodiment conductive particles can be added to the influent to thereby supply a larger amount of electricity which enables more efficient electrolyzing of large amounts of influent.

The instant invention is based on Applicants' recognition that, contrary to what is expected, the increased surface area of the electrodes does not result in an explosive condition during hydrothermal electrolysis. In this regard, it is well known in the art of electrolysis that when electricity is applied to an aqueous medium to conduct electrolysis, hydrogen gas and oxygen gas are generated at an anode and cathode, respectively. Therefore, those skilled in the art would expect that if a large amount of electricity is supplied (by increasing surface area of electrodes, for example) during hydrothermal electrolysis conducted at a high temperature and high pressure, generated hydrogen gas and oxygen gas would be mixed under a high-temperature and high-pressure condition to create a very dangerous explosive atmosphere. Accordingly, those skilled in the art would not consider increasing a surface area of electrodes in a hydrothermal electrolytic apparatus so as to increase an amount of electricity to be supplied to the apparatus while performing hydrothermal electrolysis.

The present inventors have found that generation of hydrogen gas and oxygen gas is highly suppressed during high-temperature and high-pressure hydrothermal electrolysis such that the aforementioned explosive condition does not exist. Based on this finding, the present inventors have developed a large-scale hydrothermal electrolytic apparatus having an enlarged surface area of

electrodes. Accordingly, hydrothermal electrolysis can be performed more efficiently with the inventive apparatus than with conventional apparatus, while not encountering an explosive condition resulting from mixing of oxygen gas and hydrogen gas under high pressure and high temperature.

The Examiner rejected claims 16 and 21 under 35 U.S.C. § 102(b) as being anticipated by JP '982. The Examiner rejected claims 17, 20, 22 and 25 35 U.S.C. § 103(a) as being unpatentable over JP '982 in view of JP '782. The Examiner rejected claims 18 and 23 under 35 U.S.C. § 103(a) as being unpatentable over JP '982 in view of Gilchrist. The Examiner rejected claims 19 and 24 under 35 U.S.C. § 103(a) as being unpatentable JP '982 in view of Stralser. The Examiner rejected claims 26, 32 and 33 under 35 U.S.C. § 103(a) as being unpatentable over JP '982 in view of SU '212. The Examiner rejected claims 27-29 and 34 under 35 U.S.C. § 103(a) as being unpatentable over JP '982 in view SU '212 and further in view of Hess et al. The Examiner rejected claim 30 under 35 U.S.C. § 103(a) as being unpatentable over JP '982 in view SU '212 and Hess et al., and further in view of Gilchrist. And, the Examiner rejected claim 31 under 35 U.S.C. § 103(a) as being unpatentable over JP '982 in view of SU '212 and Hess et al., and further in view of Stralser. These rejections are respectfully traversed, and the references relied upon by the Examiner are not applicable with regard to the newly added claims for the following reasons.

With regard to the newly added claims, please note that claim 35 generally corresponds to a combination of former claims 16 and 18, and that new claim 41 generally corresponds to a combination of former claims 16 and 19. Accordingly, the rejection of former claim 18 will be discussed as it pertains to new claims 35 and 47, and the rejection of former claim 19 will be discussed as it pertains to news claim 41 and 52.

The Examiner rejected claim 18 as being unpatentable over a combination of JP '982 and Gilchrist. Specifically, the Examiner recognized that JP '982 fails to disclose a reaction cell including at least two tubular reaction cells, and thus relied upon Gilchrist's teaching of tubular reaction cells as shown in Figures 6-9 for concluding that one having ordinary skill in the art would have found it obvious to have applied the method of JP '982 to the apparatus of Gilchrist. This position taken by the Examiner is respectfully traversed for the following reasons.

While JP '982 discloses the basic concept of hydrothermal electrolysis, this reference is silent with regard to any recognition that generation of hydrogen gas and oxygen gas is highly suppressed during high-temperature and high-pressure hydrothermal electrolysis. And, while Gilchrist does disclose multiple tubular electrolytic cells, Gilchrist is silent about generation of hydrogen gas and oxygen gas during electrolysis. The disclosed apparatus of Gilchrist is merely an electro-deposit apparatus that is generally operated at a temperature of 130°F -150°F (54°C - 65°C). Based on conventional knowledge in the art, one skilled in the art would have considered that use of the multiple tubular electrode construction disclosed by Gilchrist to perform the hydrothermal electrolysis of JP '982, as suggested by the Examiner, would result in a very dangerous explosive atmosphere such that one having ordinary skill in the art would not have been motivated to use the device of Gilchrist to perform the method of JP '982. Specifically, it is the high temperature and high pressure obtained during the method of JP '982 that would lead one skilled in the art to believe that an explosive situation would result were the device of Gilchrist used to practice the method of JP '982.

Accordingly, because one having ordinary skill in the art would not have been motivated to practice the method of JP '982 with the device of Gilchrist, former claim 18 and new claims 35 and 47 are not obvious for the reasons as presented by the Examiner. Thus, claims 35 and 47 are allowable. None of the other references relied upon by the Examiner resolve the above deficiencies of JP '982 and Gilchrist, and accordingly, claims 35-40 and 47-51 are allowable.

The Examiner rejected claim 19 as being unpatentable over a combination of JP '982 and Stralser. Specifically, the Examiner recognized that JP '982 fails to disclose the reaction cell as recited in former claim 19 and new claims 41 and 52, and thus took the position that in view of Stralser's teaching of a reaction cell as recited in these claims, one having ordinary skill in the art would have found it obvious to practice the method of JP '982 in the apparatus of Stralser. This position is also traversed for reasons analogous to those expressed above with regard to the combination of JP '982 and Gilchrist.

In this regard, while Stralser does disclose an electrolytic apparatus having concentrically arranged multi-tubular electrodes, Stralser is silent about generation of hydrogen gas and oxygen gas during electrolysis. The apparatus of Stralser is merely operated at a room temperature of 60°F -

80°F (15°C - 26°C). Based on conventional knowledge in the art, one having ordinary skill in the art would have considered that the use of the concentrically arranged multi-tubular electrode reaction cell of Stralser to perform the method of JP '982 would result in a very dangerous explosive atmosphere, and thus would not have considered combining JP '982 and Stralser. Specifically, it is the high temperature and high pressure obtained during the method of JP '982 that would lead one skilled in the art to believe that an explosive situation would result were the device of Stralser used to practice the method of JP '982.

Thus, claim 19 and new claims 41 and 52 are not obvious for the reasons as presented by the Examiner. The remaining references does not resolve these deficiencies of JP '982 and Stralser, and accordingly, claims 41-46 and 52 -56 are allowable.

Additionally, with regard to the Examiner's reliance on JP '782 for a teaching of providing an oxidizer line for supplying an oxidizer to the reaction cell, one having ordinary skill in the art would not have been motivated to combine the teachings of JP '982 and JP '782 because, as mentioned previously, one skilled in the art would expect addition of an oxidizer, such as oxygen, to the hydrothermal electrolysis method of JP '982 to result in a very dangerous explosive atmosphere, such that one having ordinary skill in the art would not have found it obvious to combine the teachings of JP '982 and JP '782. For this reason, claims 36, 42, 48 and 53 are patentable in their own right.

Similarly, with regard to the Examiner's reliance on SU '212 for a teaching of adding conductive particles to the electrolysis process of JP '982, because one having ordinary skill in the art would have expected the addition of such conductive particles to the process of JP '982 to result in an explosive atmosphere due to the increase of surface area of electrodes, one having ordinary skill in the art would not have sought to combine the teachings of JP '982 and SU '212. SU '212 does not teach or suggest that the conductive particles are to be added to a hydrothermal electrolysis reaction. Accordingly, claims 37, 43, 49 and 54 are patentable in their own right.

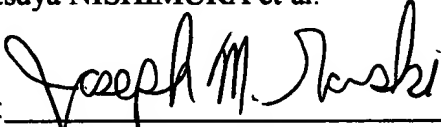
Hess et al. does not resolve any of the above deficiencies, and accordingly, claims 35-56 are allowable for the reasons as expressed above.

In view of the above amendments and remarks, it is respectfully submitted that the present application is in condition for allowance and an early Notice of Allowance is earnestly solicited.

If after reviewing this Amendment, the Examiner believes that any issues remain which must be resolved before the application can be passed to issue, the Examiner is invited to contact the Applicants' undersigned representative by telephone to resolve such issues.

Respectfully submitted,

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HYDROTHERMAL ELECTROLYTIC APPARATUS AND PROCESSES

FIELD OF THE INVENTION

[0001] The present invention relates to apparatus and processes for performing hydrothermal reaction and electrolysis at the same time. As used herein, hydrothermal electrolysis means that hydrothermal reaction and electrolysis are performed at the same time. According to the present invention, a large amount of influent containing reducible substances such as organics (including synthetic polymers) and ammonia, ~~eg, e.g.~~ organic waste liquors or various industrial waste liquors containing a halide ion ions, can be continuously treated.

PRIOR ART

55 / 01
[0002] International Application PCT/JP 98/03544 filed August 10, 1998 (International Publication WO99/07641) discloses hydrothermal electrolytic processes and apparatus previously developed by us. According to these processes and apparatus, reducible substances such as organics (including synthetic polymers) or ammonia can be effectively oxidatively degraded by performing hydrothermal reaction and electrolysis at the same time. When an oxidizer or a strong acid ion ions such as a halide ion ~~is~~ ions are contained in the an influent, hydrogen emission can be inhibited ~~in~~ during hydrothermal electrolysis. The disclosure of International Application PCT/JP 98/03544 is incorporated herein ~~as a whole as reference~~ in its entirety.

[0003] In During hydrothermal electrolysis, a closed pressure-resistant vessel is typically used as a reaction vessel because a high pressure environment is required. Thus, a batch process or a semi-continuous or continuous process consisting of repeated batch processes is applied when waste liquor is to be clarified by hydrothermal electrolysis.

[0004] However, only a small amount of waste liquor could be treated at a time and it was difficult to treat a large amount of waste liquor by a batch process or a semi-continuous process. For example, it is necessary to supply waste liquor and replace treated effluent each time in ~~the~~ a case of a batch process. However, the operation for bolting a flange or the like requires labor and care in order to perform a reaction at high temperature and high pressure. These processes are inefficient in terms of operating time or running costs.

[0005] When waste liquor is to be continuously treated, a large amount of electric power must be supplied in proportion to ~~the~~ an amount of waste liquor. Especially when a large amount of high-load influent is to be continuously treated, a quite large amount of electric power must be supplied, which may sometimes correspond to several thousands to several tens of thousands of amperes of ~~dc~~ direct current. However, it is sometimes difficult to apply several hundreds to several thousands of amperes of ~~dc~~ direct current, considering that ~~the~~ a permissive current density has a limitation depending on ~~the~~ an electrode material. As ~~the~~ a reaction vessel becomes larger, it also becomes more difficult to homogeneously supply electric power on ~~the~~ an electrode surface to homogeneously advance ~~the~~ a reaction.

[0006] Therefore, an object of the present invention is to provide a hydrothermal electrolytic apparatus capable of ~~efficiency~~ efficiently and continuously treating a large amount of waste liquor.

[0007] As a result of examinations to solve the above problems, ~~we~~ it has been found that a large amount of waste liquor can be efficiently treated by increasing ~~the~~ a surface area of electrodes in a high-pressure vessel.

DISCLOSURE SUMMARY OF THE INVENTION

5p
C2
[0008] An aspect of the present invention provides a hydrothermal electrolytic apparatus comprising a reaction cell for electrolyzing an influent containing water and reducible substances at high temperature and high pressure, wherein ~~said the~~ reaction cell defines a chamber and has a pair of electrodes and ~~the~~ an overall surface area of ~~said the~~ pair of electrodes exposed in ~~said the~~ chamber per 1 m³ of ~~the~~ volume of ~~said the~~ chamber in ~~said the~~ reaction cell is 0.05 m² or more.

[0009] Preferably, the hydrothermal electrolytic apparatus of the present invention has an inlet at ~~the~~ a bottom of the reaction cell for introducing an influent and an outlet at ~~the~~ a top of the reaction cell for discharging an effluent. This facilitates continuous treatment of influents.

[0010] Preferably, ~~said the~~ reaction cell comprises two or more tubular reaction cells each having a metal inner wall serving as a cathode, and an anode is provided in each of ~~said the tubular reaction cell~~ cells. The anode and the cathode can form ~~said the~~ pair of electrodes.

[0011] Alternatively, ~~said the~~ pair of electrodes preferably ~~have~~ has a first electrode having

two or more concentrically arranged cylindrical first side walls and a first connecting member for connecting ~~said the~~ first side walls together, and a second electrode having two or more concentrically arranged cylindrical second side walls and a second connecting member for connecting ~~said the~~ second side walls together, wherein ~~said the~~ first side walls of ~~said the~~ first electrode and ~~said the~~ second side walls of ~~said the~~ second electrode are alternately arranged to form a channel for influent between ~~said the~~ first side walls and ~~said the~~ second side walls.

[0012] Moreover, the hydrothermal electrolytic apparatus of the present invention preferably further has a high-pressure pump, an influent line for supplying influent to ~~said the~~ reaction cell, an oxidizer line for supplying an oxidizer to ~~said the~~ reaction cell, and an effluent line for discharging effluent from ~~said the~~ reaction cell.

SD
C3
[0013] Another aspect of the present invention provides a process for preparing clarified water, comprising the steps of introducing an influent containing water and reducible substances into a reaction cell of ~~said a~~ hydrothermal electrolytic apparatus, supplying a direct current into ~~said the~~ reaction cell at a temperature of between 100°C or more but the and a critical temperature of said the influent or less and at a pressure that allows water in ~~said the~~ influent to be kept maintained in the a liquid phase, and discharging an effluent from ~~said the~~ reaction cell. This clarified water may be recycled to another process or discharged to ~~the an~~ environment.

[0014] Preferred embodiments of the present invention are explained in detail below with reference to the attached drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] FIG. 1 is a longitudinal sectional view showing ~~the an~~ inner structure of ~~the a~~ reaction vessel forming ~~the a~~ core of a hydrothermal electrolytic apparatus according to a first embodiment of the present invention.

[0016] FIG. 2 is a cross-sectional view showing the inner structure of the reaction vessel according to the first embodiment.

[0017] FIG. 3 is an enlarged sectional view of B in FIG. 1.

[0018] FIG. 4 is an enlarged cross-sectional view showing a partial inner structure of C in

FIG. 1.

[0019] FIG. 5 is a longitudinal sectional view showing ~~the~~ an inner structure of ~~the~~ a reaction vessel forming ~~the~~ a core of a hydrothermal electrolytic apparatus according to a second embodiment of the present invention.

[0020] FIG. 6 is a cross-sectional view showing the inner structure of the reaction vessel according to the second embodiment.

[0021] FIG. 7 is an enlarged sectional view of E in FIG. 5.

[0022] FIG. 8 is an enlarged sectional view of F in FIG. 6.

[0023] FIG. 9 is an enlarged sectional view of G in FIG. 5.

[0024] FIG. 10 shows a variant of the first embodiment of the present invention.

[0025] FIG. 11 is a cross-sectional view showing ~~the~~ an inner structure of the reaction vessel in of the variant of the first embodiment of the present invention shown in FIG. 10.

[0026] FIG. 12 shows another variant of the first embodiment of the present invention.

[0027] FIG. 13 is a schematic view of a hydrothermal electrolytic treatment system of the present invention.

[0028] FIG. 14 is a schematic view of a hydrothermal electrolytic treatment system according to a third aspect of the present invention.

[0029] FIG. 15 is a schematic view of ~~the~~ an experimental apparatus for a hydrothermal electrolytic process of the present invention used in Example 1.

~~THE MOST~~ DESCRIPTION OF THE PREFERRED EMBODIMENTS ~~OF THE~~ INVENTION

[0030] Fig. 1 is a longitudinal sectional view showing ~~the~~ an inner structure of reaction vessel 1 forming ~~the~~ a core of ~~the~~ a hydrothermal electrolytic apparatus according to a first embodiment of the present ~~invention;~~ invention. Fig. 2 is a widthwise sectional view showing the inner structure of the reaction vessel. Fig. 3 is an enlarged sectional view of B in Fig. 1. Fig. 4 is an enlarged sectional view of C in Fig. 2 1. Fig. 4 shows a section of ~~the~~ a part at which a spacer 43 is provided.

[0031] As shown in Figs. 1-4, the hydrothermal electrolytic apparatus according to this

embodiment comprises a reaction cell 31 for electrolyzing an influent containing water at high temperature and high pressure. ~~Reaction~~ The reaction cell 31 defines chambers 7 and each of which has a pair of electrodes 31a, 41. ~~Thus, the~~ An inner face of reaction cell 31 defining chamber 7 can serve as electrode 31a. ~~The~~ An overall surface area of ~~a~~ the pair of electrodes 31a, 41 exposed in chamber 7 ~~in of the~~ in the reaction cell 31 per 1 m³ of ~~the~~ a volume of the chamber is 0.05 m² or more, preferably 0.1 m² or more, more preferably 0.2 m² or more. The "overall surface area of electrodes" here means ~~the~~ an effective surface area of electrodes substantially participating in an electrolytic reaction.

[0032] If the overall surface area of ~~a~~ the pair of electrodes 31a, 41 is less than 0.05 m², enough electric power ~~can not~~ cannot be supplied to ~~the~~ influent for rapid hydrothermal electrolysis.

[0033] In the first embodiment of the present invention shown in Fig. 1, the reaction cell consists of two or more tubular reaction cells 31. Each of tubular reaction cells 31 has provided therein a metal inner wall 31a serving as a cathode, and a discharge electrode 41 serving as an anode ~~is provided in each of said reaction cells 31.~~

[0034] The first embodiment of the present invention comprises ~~a~~ reaction vessel 1. Reaction vessel 1 comprises a lower vessel part 2, a middle vessel part 3 and an upper vessel part 4. Lower vessel part 2 comprises an inlet 21 for introducing influent, an oxidizer inlet 22 for introducing an oxidizer, and a mixing chamber 23 for mixing the influent introduced from inlet 21 with the oxidizer introduced from oxidizer inlet 22. Middle vessel part 3 comprises tubular reaction cells 31 in which the influent mixed with ~~an~~ the oxidizer is electrolyzed under pressure and ~~heating~~ heat.

[0035] Upper vessel part 4 comprises a current feed terminal 42 corresponding to each reaction cell 31. Current feed terminal 42 preferably has an insulating member extending from reaction vessel 1. Each current feed terminal 42 has a discharge electrode 41 extending to ~~the inside~~ an interior of reaction cell 31.

[0036] Lower vessel part 2, middle vessel part 3 and upper vessel part 4 are connected together via gaskets 5, which tightly seal ~~the inside~~ interiors of these vessel parts. Thus, reaction vessel 1 as a whole forms a pressure-resistant vessel.

[0037] Each of inlet 21 and oxidizer inlet 22 is singly provided in a wall portion 2a on ~~the~~ a bottom of lower vessel part 2. Inlet 21 is connected to an influent line and oxidizer inlet 22 is connected to an oxidizer line.

[0038] Mixing chamber 23 is partitioned by a dispersion plate 24 and contains a stirrer 25 therein. Dispersion plate 24 may be of any known means type for mixing ~~the~~ the influent by disturbing ~~the~~ a flow thereof. Stirrer 25 is a common type having stirring blades 25a and is used to help in mixing influent, and is connected to a motor ~~not shown~~ (not shown).

[0039] At ~~the~~ a connection between lower vessel part 2 and middle vessel part 3 is provided an introducing chamber 6 for smoothly introducing ~~the~~ the influent, mixed with an oxidizer in mixing chamber 23, into the reaction cell 31. Wall 3a of middle vessel part 3 is connected to a negative line 32, which is in turn connected to a negative terminal ~~not shown~~ (not shown) of a ~~dc~~ direct current source at constant current and voltage.

[0040] ~~The tubular body~~ Tubular bodies forming the tubular reaction cell ~~cells~~ 31 ~~is~~ are electrically connected with wall 3a of middle vessel part 3. For example, a stainless steel ~~tube~~ tubes may be welded to a stainless steel middle vessel part 3. Thus, ~~the entire~~ inner face 31a of reaction cell 31 in its entirety serves as a cathode. ~~Reaction~~ Each reaction cell 31 may be integrally formed with middle vessel part 3, or separately formed and fitted or otherwise incorporated into it the middle vessel part. Thus, ~~the~~ inner face 31a of reaction cell 31 serves as a negative electrode to prevent corrosion by electrolysis.

[0041] Discharge electrode 41 is in the form of a rod having a diameter smaller than ~~the~~ an inner diameter of reaction cell 31 and is arranged at a predetermined position in such a manner that each one ~~may be~~ is inserted into each reaction cell 31. ~~The~~ Each discharge electrode 41 may be a cylindrically shaped mesh or net, or a cylinder having an axial hollow.

[0042] In the present invention, ~~the~~ a distance between the anode and the cathode is preferably equal. If this distance varies, an excessive current flows locally at narrow regions to accelerate deterioration of the anode at ~~those~~ these regions. In this embodiment, inner wall 31a of reaction cell 31 preferably has a cylindrical shape. Preferably, ~~the~~ an outer peripheral face of

discharge electrode 41 also has a cylindrical shape so that ~~the center~~ a central axis of discharge electrode 41 substantially coincides with ~~the center~~ a central axis of inner wall 31a of reaction cell 31.

[0043] At an end of discharge electrode 41 is provided an insulating spacer 43 to prevent any contact of the discharge electrode with the an inner face of reaction cell 31. Insulating spacer 43 is preferably formed to suit the a shape of the an outer surface of discharge electrode 41 and the a shape of the an inner face of reaction cell 31. Insulating spacer 43 preferably has a through hole that allows the influent to pass therethrough.

[0044] Current feed terminal 42 is connected to a positive line 44, which is in turn connected to a positive terminal ~~not shown~~ (not shown) of a constant ~~dc~~ direct current source separately provided. Thus, discharge electrode 41 serves as an anode.

[0045] A chamber 7 is formed between the inner face of each reaction cell 31 and its corresponding discharge electrode 41, and is connected to a discharge channel 8 formed at the a connection between middle vessel part 3 and upper vessel part 4. Discharge channel 8 is connected to an outlet 34 at the an upper end of middle vessel part 4 3 for discharging effluent from reaction vessel 1.

[0046] Thus, the reaction vessel in the hydrothermal electrolytic apparatus according to this embodiment has an inlet at the bottom for introducing an influent and an outlet at the top for discharging an effluent. This makes it easier to continuously hydrothermally electrolyze an influent. The reaction vessel has a plurality of rod-like discharge electrodes and the same number of tubular reaction cells.

[0047] As used herein, the "volume of the chamber in the reaction cell" does not include the a volume of discharge electrode 41 in reaction cell 31, but means the a volume of the a part where an influent is electrolyzed at high temperature and high pressure. In this embodiment, it specifically means the a volume of chamber 7 located between electrodes 31a, 41 in reaction cell 31.

[0048] In this embodiment, the "overall surface area of a pair of electrodes exposed in the chamber" means the total of the a surface area of electrode 31a and the a surface area of discharge electrode 41 exposed in chamber 7. This excludes the an area of discharge electrode 41 not exposed in chamber 7, eg e.g., the a surface area of the a part of the discharge electrode located within upper

vessel part 4, or the a surface area of the a part of the discharge electrode exposed in discharge channel 8, because these parts do not participate in the electrolysis of an influent.

[0049] Each member can be formed from any material so far long as middle vessel part 3 and each reaction cell 31 ~~should be~~ are formed from an electrically conductive material, and the reaction vessel as a whole ~~should be~~ is formed from a heat-resistant and pressure-resistant material. For example, middle vessel part 3 and each reaction cell 31 can be formed from stainless steel. ~~Reaction~~ Each reaction cell 31 may have a multilayer structure comprising the an innermost layer of an electrically conductive material such as stainless steel and ~~the~~ other layers of ceramics.

[0050] The hydrothermal electrolytic apparatus according to this embodiment can be used as follows.

[0051] An influent is heated up to a ~~subcritical~~ sub-critical temperature and then introduced via inlet 21. At the same time, an oxidizer such as oxygen-dissolved water is introduced via oxidizer inlet 22 and mixed with the influent in mixing chamber 23. The influent mixed with the oxidizer is forced upward upwardly under the pressure of successively introduced influent and oxidizer and inserted into reaction ~~cell~~ cells 31 via lower ~~opening~~ openings 31b of ~~the reaction cell 31~~ cells. The influent introduced into reaction ~~cell~~ cells 31 is subjected to hydrothermal reaction and electrolytic oxidation reaction as it moves ~~in chamber~~ through chambers 7 so that reducible substances in the influent are degraded. ~~The treated~~ Treated influent is introduced into discharge channel 8 via upper ~~opening~~ openings 31c and discharged from outlet 34. ~~The effluent~~ Effluent, after treatment, is introduced into various tanks as in known processes. In the apparatus according to this embodiment, a series of these reaction processes can be continuously performed.

[0052] The hydrothermal electrolytic apparatus according to this embodiment has the an advantage in that a large amount of influent can be treated because the reaction vessel has electrodes of a specific area as described above, which increases the throughput and advances a homogeneous reaction. Moreover, this embodiment allows a large amount of influent to be continuously treated even while using a reaction vessel having an inlet at the a bottom and an outlet at the a top because ~~said these~~ electrodes have a specific area. This embodiment also has the an advantage in that current feed terminals are easily mounted to improve workability.

[0053] Therefore, the apparatus of the present invention improves the efficiency of

hydrothermal electrolytic reaction to effectively use the input energy and also reduces the size of the apparatus by increasing the surface area of electrodes per volume of chambers.

[0054] Next, a second embodiment of the present invention is explained with reference to Figs. 5-9, in which Fig. 5 is a longitudinal sectional view showing the inner structure of the reaction vessel forming the core of the hydrothermal electrolytic apparatus according to the second embodiment of the present invention, Fig. 6 is a widthwise sectional view showing the inner structure of the reaction vessel, Fig. 7 is an enlarged sectional view of E in Fig. 5, Fig. 8 is an enlarged sectional view of F in Fig. 6, and Fig. 9 is an enlarged sectional view of G in Fig. 5. In the following description, differences from the first embodiment are described especially in detail. The foregoing explanation about the first embodiment is appropriately applied when no special reference is made.

[0055] In the second embodiment shown in Figs. 5-9, lower vessel part 2 has an influent inlet 21 at the center of the central bottom portion, and a pipe 26 is connected to inlet 21 to extend upwardly from lower vessel part 2 to middle vessel part 3. Influent has been preliminarily mixed with an oxidizer in a mixer ~~not shown~~ (not shown), if desired. Preferably, influent has been preliminarily heated up to a temperature of at least 100°C or more but below the critical temperature of the influent or less.

[0056] Middle vessel part 3 includes an anode 35a and a cathode 35b. Anode 35a (first electrode) has two or more concentrically arranged cylindrical side walls 37a (first side walls) and a connecting member 36a (first connecting member) for connecting side walls 37a together. In the same manner, cathode 35b (second electrode) has two or more concentrically arranged cylindrical side walls 37b (second side walls) and a connecting member 36b (second connecting member) for connecting side walls 37b together. Side walls 37a of anode 35a and side walls 37b of cathode 35b are alternately arranged to form a channel for influent between side walls 37a and 37b.

[0057] Preferably, pipe 26 is electrically connected to connecting member 36b to serve as cathode 35b. Thus, pipe 26 and the reaction vessel body can be protected against corrosion by cathodic protection.

[0058] Both connecting members 36a, 36b are in the form of a disk and are electrically

conductive. Connecting member 36a fixes anode 35a to current feed terminals 42. Connecting member 36b fixes cathode 35b to lower vessel part 2.

[0059] Thus, the hydrothermal electrolytic reactor according to this embodiment has a concentrically arranged cylindrical continuous reaction channel. The reaction channel is continuously provided from ~~the a~~ center to ~~the an~~ outer periphery of the reaction vessel so that influent flows from the center to the outer periphery of the reaction vessel. Upper vessel part 4 includes a plurality of current feed terminals 42. Upper vessel part 4 and current feed terminals 42 are electrically insulated from each other via an insulator 42a, as shown in Fig. 9.

[0060] In this embodiment, the "volume of chambers in the reaction cell" means ~~the a~~ volume of ~~the a~~ part where ~~the~~ influent is hydrothermally electrolyzed in middle vessel part 3. The "volume of chambers in the reaction cell" excludes ~~the a~~ volume of anode 35a, ~~the a~~ volume of cathode 35b and ~~the a~~ volume defined by pipe 26.

[0061] When pipe 26 serves as a cathode, radially outer channels of pipe 26 are included in the chamber. When pipe 26 is not electrically conductive and does not serve as ~~an electrode a~~ cathode, however, radially outer channels of pipe 26 are not included in the chamber.

[0062] In the apparatus according to this embodiment, influent is introduced from inlet 21 and transferred to ~~the a~~ top of the reaction vessel through pipe 26, then transferred from the top to ~~the a~~ bottom of the reaction vessel in ~~the~~ through an outer channel, then transferred from the bottom to the top in ~~the a~~ subsequent outer channel, and so on. Thus, it influent is transferred successively from the center to the periphery of the reaction vessel. During ~~then~~ this transfer, reducible substances in the influent are oxidatively degraded by hydrothermal electrolysis. ~~The treated~~ Treated influent is discharged from outlet 34 to ~~the outside~~ an exterior of the reaction vessel †.

[0063] In addition to ~~the same~~ advantages as obtained in the first embodiment, the apparatus according to this embodiment also has ~~the an~~ an advantage in that ~~the a~~ reaction channel can be longer so as to improve ~~the~~ efficiency of electrolysis. Thus, even low-concentration influents can be effectively treated.

[0064] Hydrothermal electrolytic apparatus according to the first and second embodiments

are not limited to the foregoing embodiments, but and can be modified in various respects without departing from the spirit of the present invention.

[0065] For example, a mixing chamber having a stirrer was illustrated in the first embodiment, but the mixing chamber may not be necessary as shown in the second embodiment. The mixing chamber may not necessarily have a stirrer or a dispersion plate so far long as the influent and oxidizer, or the like, are mixed with one another.

[0066] The embodiment shown in Figs. 2 and 3 may be replaced by the embodiment shown in Figs. 10 and 11. That is, a heat-insulating material 39 may be filled outside of reaction ~~cell~~ cells 31 in middle vessel part 3.

[0067] Alternatively, the reaction vessel may be thermally insulated by evacuation from a vacuum pump via a port formed in middle vessel part 3 instead of using an insulating material.

[0068] Alternatively, ~~the a~~ temperature may be kept maintained by providing a heater 45 on ~~the an~~ outer peripheral face of middle vessel part 3 as shown in Fig. 12. Ports 46 and 47 may be further provided in middle vessel part 3 as shown in Fig. 12. Thus, the temperature can be kept maintained to be constant by directly heating ~~the inside~~ an interior of middle vessel part 3 with a thermal fluid flown from port 46 into middle vessel part 3. The thermal fluid is discharged from port 47. The thermal fluid may be used not only for heating but also for cooling.

[0069] It is useful to provide a heater on the outer peripheral face of middle vessel part 3 as shown in Fig. 12 especially in the second embodiment in which ~~the~~ temperature of ~~the an~~ influent may be lowered as ~~it closes to the~~ influent approaches a peripheral face of the vessel.

[0070] Next, materials of members, reaction conditions or the like that can be used in the present invention are described. In hydrothermal electrolytic apparatus of the present invention, the discharge electrode or anode preferably has a surface having ruthenium, iridium, platinum, palladium, rhodium, tin or an oxide thereof or a ferrite. For example, the discharge electrode itself may be made from any of these materials. Alternatively, ~~the a~~ base material of the discharge electrode may be coated with any of these materials ~~on the surface~~.

[0071] Ruthenium, iridium, platinum, palladium, rhodium and tin may be elemental metals or

oxides. Alloys of these metals are also preferably used. Such alloys include, for example, platinum-iridium, ruthenium-tin and ruthenium-titanium. These metals show high corrosion resistance, and excellent insolubility for use as an anode. In some preferred embodiments, especially preferred electrodes are based on palladium, ruthenium or an alloy of platinum and iridium.

[0072] During the hydrothermal electrolytic reaction of the present invention, the current density at the a surface of the an anode is preferably $0.1 \text{ mA/dm}^2 - 500 \text{ A/dm}^2$. If the current density is higher than 500 A/dm^2 , the a surface of the anode is liable to be exfoliated or dissolved. If the current density is lower than 0.1 mA/dm^2 , however, the an area of the anode must be increased and thus the system becomes bulky. The current density is more preferably $10 \text{ mA/dm}^2 - 100 \text{ A/dm}^2$, most preferably $100 \text{ mA/dm}^2 - 50 \text{ A/dm}^2$. If a new material for the anode is developed, the current density at the anode can be further increased.

[0073] In hydrothermal electrolytic apparatus and processes of the present invention, an influent containing water and reducible substances can be treated to oxidatively degrade the reducible substances. Influent s that can be treated by the present invention include various waste liquors. Reducible substances that can be degraded by the present invention include organics and ammonia. Examples of organics include aliphatic and aromatic hydrocarbons such as alkanes, alkenes, alkynes; alcohols; aldehydes; ketones; amines; carboxylic acids such as acetic acid; carboxylic acid derivatives such as esters, amides, anhydrides; halogenated hydrocarbons; phenols; sulfur-containing organic compounds such as sulfoxides, mercaptans, thiols, polysulfones; etc and the like. Organics also include synthetic polymers such as polyolefins, polyesters or various engineering plastics.

[0074] Influent s preferably have fluidity, and may be any of suspension, emulsion, aqueous solution or slurry, but preferably suspension or slurry. Influent s may contain liquid or solid reducible substances. Influent s include suspensions of unprecipitable solid particles dispersed in water, emulsions of liquid particles dispersed in water, aqueous solutions of liquid organics or inorganics dissolved in water and mixtures thereof. For example, influent s contain a continuous phase containing water, liquid organics and dissolved salts and a discontinuous phase containing solid organics such as particles, and optionally non-combustible solids such as ash.

[0075] Preferably, influent s contain a strong acid ion ions. This is because strong acid ions show an electrochemical catalytic effect to advance hydrothermal electrolytic reaction more

efficiently. The strong acid ~~ion ions~~ may be ~~an~~ inorganic acid ~~ion ions~~ or ~~an~~ organic acid ~~ion ions~~. However, the strong acid ~~is ions are~~ preferably ~~an~~ inorganic acid ~~ion ions~~ because organic acid ions may be degraded as hydrothermal electrolysis proceeds.

[0076] Suitable inorganic strong acid ions include, for example, halide ions, sulfate ~~ion ions~~ (SO_4^{2-}), nitrate ~~ion ions~~ (NO_3^-), phosphate ~~ion ions~~ (PO_4^{3-}), among which halide ions are especially preferred. Suitable organic strong acid ions include, for example, trifluoroacetate ~~ion ions~~ (CF_3COO^-).

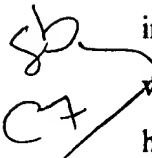
[0077] Suitable halide ions include chloride ~~ion ions~~ (Cl^-), bromide ~~ion ions~~ (Br^-), iodide ~~ion ions~~ (I^-) or any combination thereof, among which chloride ~~ion ions~~ or bromide ~~ion-is ions are~~ are especially preferred. A halide ion-producing salt may be dissolved in the ~~an~~ influent. A hydrohalic acid such as hydrogen chloride (HCl), hydrogen bromide (HBr) or hydrogen iodide (HI) may be contained in the ~~an~~ influent. When the ~~an~~ influent contains polyvinyl chloride, chloride ~~ion moves ions move~~ to the ~~an~~ aqueous phase to incorporate chloride ~~ion ions~~ as hydrothermal reaction proceeds.

[0078] In ~~For~~ hydrothermal electrolysis according to the present invention, an oxidizer is preferably added to the ~~an~~ influent to more efficiently advance hydrothermal electrolytic oxidation. Oxidizers that can be used in the present invention are oxygen gas, ozone gas, hydrogen peroxide and hypohalous acids, more preferably oxygen gas. Oxygen gas may be a gas containing oxygen gas, ~~eg,~~ e.g. air is preferably used. Thus, air can be bubbled into water or the like to dissolve oxygen, and the ~~a~~ resulting oxygen-dissolved water can be introduced as an oxidizer via oxidizer inlet 22. Alternatively, compressed air can be introduced into reaction cell 23 to serve as an oxidizer.

[0079] In ~~During~~ hydrothermal electrolysis according to the present invention, hydrothermal reaction takes place at a temperature of ~~between~~ 100°C ~~or more but the~~ and a critical temperature of ~~said an~~ influent, ~~or less~~ and at a pressure that allows ~~said the~~ influent to be ~~kept~~ in the ~~a~~ liquid phase. Temperatures lower than 100°C are not preferred because the ~~a~~ rate of hydrothermal reaction is lowered to extend the ~~a~~ reaction time. However, the ~~a~~ finding of the present invention cannot be directly applied for temperatures higher than the critical temperature because physical properties of aqueous medium significantly change at this temperature. At the ~~a~~ supercritical super-critical stage, for example, the solubility of the ~~electrolyte electrolytes~~ greatly decreases and electric conductivity is decreased.

[0080] Next, a specific arrangement of an influent treatment system using a hydrothermal electrolytic reactor according to the present invention is explained with reference to Fig. 13. Fig. 13 shows such an influent treatment system. In the treatment system shown in Fig. 13, an influent line 60 for supplying an influent is connected to a hydrothermal electrolytic reaction vessel 1 of the present invention. Influent line 60 preferably has a feed tank 61, a high-pressure pump 66, a heat exchanger 70 and a heater 74, and an influent can be transferred through these components in this order. Hydrothermal electrolytic reaction vessel 1 may consist of a hydrothermal electrolytic reaction vessel according to the first embodiment, a hydrothermal electrolytic reaction vessel according to the second embodiment, or the like.

[0081] Feed tank 61 can hold an influent. To feed tank 61 are connected a wastewater line 62 for introducing wastewater into feed tank 61 and a halide line 63 for supplying a halide ion source, such as chloride ~~ion~~ ions (Cl^-), into feed tank 61. This halide ion source may be sea water. Halide line 63 can supply a halide ~~ion~~ ions such as chloride ~~ion~~ ions to feed tank 61 so as to control ~~the~~ a halide ion level in the influent held in feed tank 61.

**[0082]** Feed tank 61 can be connected to high-pressure pump 66 via line 64 to transfer an influent. A tap water line 68 for supplying tap water is preferably connected to line 64 so that tap water, substantially free from reducible substances, can be transiently ~~flown~~ flowed when the hydrothermal electrolytic apparatus shown in Fig. 13 is started up or stopped.

[0083] High-pressure pump 66 pressurizes the influent to a pressure required for hydrothermal reaction so as to force the influent into reaction vessel 1 under this pressure via heat exchanger 70 and heater 74.

[0084] Influent line 60 preferably has heat exchanger 70. Heat exchanger 70 is connected to influent line 60 and effluent line 100 so that heat exchanger 70 ~~changes~~ exchanges heat between the influent flowing in influent line 60 and the effluent flowing in effluent line 100. ~~The influent~~ Influent pressurized in high-pressure pump 66 is often at room temperature. However, the effluent discharged from reaction vessel 1 is ~~kept~~ maintained at high temperature via hydrothermal reaction. Therefore, heat exchanger 70 heats the influent flowing in influent line 60 and cools the effluent flowing in effluent line 100. Even if the heat exchanger is not provided, only heat efficiency decreases.

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[0085] Preferably, influent line 60 has a heater 74 for further heating the influent heated by heat exchanger 70. Especially when reaction vessel 1 has a large diameter, it is inefficient to heat influent 52 in reaction vessel 1 from the outside an exterior of reaction vessel 1, and it is thus preferable to provide heater 74 in the influent line. Heater 74 heats the influent to a temperature required for hydrothermal reaction, for example. The A temperature to which the influent is heated is determined taking into account the exothermic heat from the an oxidation reaction, and the exothermic heat from the electrolysis of reducible substances in reaction vessel 1. Another heater for heating the outside an exterior of reaction vessel 1 may also be further provided.

[0086] Separately from influent line 60, an oxidizer line 80 is preferably provided. Suitable oxidizers include gases containing oxygen gas such as air. Air is introduced into compressor 82 via line 81 and preferably pressurized from 1 MPa to 25 MPa, for example. This compressed air is introduced into accumulator 84 via line 83. Thus, compressor-induced pulsation of compressed air can be prevented.

[0087] A valve 85 for controlling the an amount of compressed air, ~~ie, the~~ i.e. an amount of oxidizer, is provided downstream of accumulator 84. Compressed air is preheated in heat exchanger 87 and then introduced into reaction vessel ~~150 via line 188~~ 1. Heat exchanger ~~187~~ 87 heats compressed air and cools the effluent.

[0088] Alternatively, a liquid such as water, in which oxygen gas is dissolved, may be introduced into reaction vessel 1. Oxidizers in the a form of a gas such as oxygen gas (including air) have higher water-solubility at lower temperature or higher pressure. Therefore, an oxidizer in the form of a gas may be dissolved in water at low or room temperature under high pressure, and then this cold water may be supplied to the reaction vessel. Alternatively, aqueous hydrogen peroxide, a hypochlorous acid or a solid oxidizer may be dissolved in water and supplied to the reaction vessel via a high-pressure pump or the like. When an oxidizer rich in water is added, an additional heater may be provided between high-pressure pump 86 and reaction vessel 1.

[0089] Preferably, oxidizer line 80 is directly connected to reaction vessel 1. If oxidizer line 80 is connected to influent line 60, line 76 between heater 74 and reaction vessel ~~50~~ 1 will be susceptible to corrosion. On the ~~another~~ other hand, when an oxidizer is directly introduced into

reaction vessel 1, ~~the~~ an inner wall of reaction vessel 1 can be protected from corrosion because the inner wall of reaction vessel ~~11~~ 1 serves as a cathode ~~of~~ for electrolysis.

[0090] Reaction vessel 1 may consist of a reaction vessel according to the first or second embodiment as described above. Preferably, reaction vessel 1 has an axially extending tubular shape, preferably a cylindrical shape. Positive terminal 96 and negative terminal 97 of ~~de~~ direct current source 94 are connected to ~~the~~ an anode and ~~the~~ a cathode of ~~hydrothermal-electrolytic apparatus~~ reaction vessel 1 via lines 98, 99, respectively.

[0091] In the embodiment shown in Fig. 13, an effluent line 100 for discharging the hydrothermally electrolyzed influent is connected to reaction vessel 1. Preferably, effluent line 100 has heat exchangers 70/87, a gas-liquid separator 102, and an effluent tank 110, and the effluent hydrothermally electrolyzed in reaction vessel 1 can be transferred through these components in this order. Heat exchangers 70/87 have already been explained.

[0092] Preferably, gas-liquid separator 102 is connected to effluent line 100. Gas-liquid separator 102 separates gas and liquid in ~~the~~ an effluent. The effluent is held at a predetermined level 104 in gas-liquid separator 102. ~~Pressure~~ A pressure transmitter tube may be provided between ~~the~~ a space above ~~said~~ level 104 and ~~the~~ effluent below ~~said~~ level 104, and a level ~~detector~~; detector for determining ~~the~~ a gas-liquid interface or slurry ~~level~~; level may be provided in this pressure transmitter tube. Level-detecting mechanism 106 may be designed to measure ~~the~~ level 104 by ~~the~~ a pressure difference between gas and liquid to discharge the effluent in such a manner that ~~said~~ level 104 may be fixed or within a fixed range. Gas-liquid separator 102 may be provided with a piezoelectric element, for converting pressure into an electric signal, both ~~each~~ above and below ~~said~~ level 104, whereby this electric signal is entered into a level detector to detect the pressure difference.

[0093] Preferably, gas-liquid separator 102 has ~~a~~ level-controlling mechanism 106 for stabilizing ~~the~~ a level of the effluent in gas-liquid separator 102 within a fixed range. ~~Said~~ This level-controlling mechanism may have a level detector for detecting ~~the~~ a pressure difference between gas and the effluent, a valve for discharging the effluent, and a controller for controlling the valve by a signal from the level detector. The level-controlling mechanism may have a pressure transmitter tube or a piezoelectric element.

[0094] A valve 108 is connected to gas-liquid separator 102 so that ~~the~~ effluent in gas-liquid

separator 102 can be discharged into container 110 when valve 108 is opened. Preferably, switching of valve 108 is controlled by a signal from level-controlling mechanism 106.

[0095] Gas-liquid separator 102 may have a pressure controlling mechanism for controlling the pressure in the gas-liquid separator within a predetermined range. ~~Said~~ This pressure controlling mechanism may have, for example, a pressure detector for detecting the pressure of the a gas phase, a valve for discharging gas, and a controller for controlling the valve by a signal from the pressure detector. The pressure-controlling mechanism controls the pressure in the a range so that the influent is ~~kept at the~~ maintained in a liquid phase, and reaction vessel 1 and gas-liquid separator 102 are safely operated, for example. The pressure detector may have a piezoelectric element.

[0096] A valve 109 is connected to gas-liquid separator 102 so that the gas in gas-liquid separator 102 can be discharged to the an atmosphere when valve 109 is opened. Preferably, switching of valve 109 is controlled by a signal from a pressure-controlling mechanism ~~not shown~~ (not shown).

[0097] Next, a hydrothermal electrolytic process using the hydrothermal electrolytic treatment system shown in Fig. 13 is explained.

[0098] Explanation begins with the operation at start-up. Suppose that no liquid has been introduced into reaction vessel 1 yet. Tap water is first introduced into influent line 60 from tap water line 68 at room temperature and atmospheric pressure. Tap water is transferred through heat exchanger 70, heater 74 and then reaction vessel 1 by high-pressure pump 66. After tap water is introduced into heater 74, heater 74 is activated to heat the tap water. Thus, heated tap water is discharged from reaction vessel 1 to effluent line 100 and then discharged into container 110 via gas-liquid separator 102.

[0099] After the system is stabilized, tap water supply from the tap water line to influent line 60 is stopped and influent supply from feed tank 61 to influent line 60 is started. Halide ion level, or other the like, of the influent ~~are~~ is preliminarily controlled via halide line 63 or the like. The influent is introduced into reaction vessel 1 while heating of the influent is continued in heater 74. An oxidizer is introduced into reaction vessel 1 via oxidizer line 80.

[0100] After the influent and oxidizer are introduced into reaction vessel 1, electrolysis is started. Thus, ~~dc~~ direct current source 94 is turned on to supply ~~dc~~ direct current to the anode and cathode of ~~hydrothermal electrolytic apparatus~~ reaction vessel 1. The influent ~~kept maintained~~ in the a liquid phase under high temperature and high pressure moves in through reaction vessel 1, during which hydrothermal reaction and electrolysis proceed at the same time. ~~The~~ A heating temperature of heater 74 is appropriately lowered because heat is generated with hydrothermal reaction and electrolysis.

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[0101] ~~The~~ A reaction time should be enough long for reducible substances in the influent to be oxidatively degraded, for example 1 second to 48 hours, preferably 1 minute to 24 hours. The reaction time is more preferably 5 hours or less, still more preferably 2 hours or less. The reaction time is adjusted in as a function of ~~the~~ volume of reaction vessel 1 and ~~the~~ feed flow rate of the influent.

[0102] When the a reaction is to be stopped, ~~the~~ inflow from feed tank 61 to influent line 60 is stopped and tap water is introduced from the tap water line to influent line 60. Oxidizer supply from oxidizer line 80 into reaction vessel 1 is also stopped. Then, the ~~dc~~ direct current source is turned off to stop electrolysis. Then, ~~the~~ an output of heater 74 is lowered so that ~~the~~ a temperature of the influent flowing into reaction vessel 1 is gradually lowered.

[0103] According to the first and second embodiments of the present invention, influent can be efficiently treated by hydrothermal electrolytic reaction by increasing the a surface area of electrodes in for hydrothermal electrolysis, as has been described above.

[0104] However, it is not always easy to increase the surface area of electrodes as desired because the surface area of electrodes cannot be indefinitely increased in a limited space of the reaction vessel even by the above approach.

[0105] Thus, ~~we~~ also ~~provide~~ provided is a process and an apparatus for substantially increasing the a surface area of electrodes easily and inexpensively as alternatives to the foregoing embodiments.

[0106] Namely, ~~we~~ it has been found that the surface area of electrodes can be substantially increased by incorporating electrically conductive particles into ~~the~~ an influent, preferably suspending

electrically conductive particles ~~into~~ in the influent so that the conductive particles present in the influent can substantially serve as an electrode during the electrolysis of the influent.

[0107] ~~The incorporation~~ Incorporation of electrically conductive particles into the influent means that the influent containing water and electrically conductive particles is located between ~~the~~ an original cathode and ~~the~~ an original anode in ~~the~~ a hydrothermal electrolytic apparatus. When a ~~de~~ direct current voltage is applied across the original cathode and the original anode, individual conductive particles serve as an anode at ~~the~~ surfaces facing the original cathode, and serve as a cathode at ~~the~~ surfaces facing the original anode under ~~the~~ an effect of an electric field. Therefore, a current flows locally between the original cathode and ~~the~~ surfaces of individual conductive particles serving as an anode, and also a current flows locally between the original anode and ~~the~~ surfaces of conductive particles serving as a cathode. When two conductive particles are located in proximity to but ~~without~~ not in contact ~~with,~~ with each other, and ~~the~~ a cathodic surface of one conductive particle faces ~~the~~ an anodic surface of the other conductive particle, for example, a current flows locally between the cathodic surface and the anodic surface. This also applies to more than two discrete conductive particles, in which case a current seems to flow between ~~the~~ a cathodic surface of a conductive particle and ~~the~~ an anodic surface of another conductive particle.

[0108] Thus, ~~the~~ current flowing between the original anode and the original cathode increases and ~~the~~ a voltage across the original anode and the original cathode also increases when conductive particles exist in ~~the~~ an influent as compared ~~with~~ to when no conductive particles exist in the influent. Therefore, a large amount of electric power can be supplied to the influent to greatly improve ~~the~~ throughput and process efficiency of the hydrothermal electrolytic apparatus without increasing ~~the~~ a surface area of the original anode and the original cathode.

[0109] Accordingly, a third aspect of the present invention provides a hydrothermal electrolytic process comprising ~~the~~ a step of subjecting an influent containing water, reducible substances and conductive particles to electrolysis at a temperature of between 100°C ~~or more but~~ the and a critical temperature of ~~said~~ the influent, ~~or less~~ and at a pressure that allows water in ~~said~~ the influent to be kept maintained in ~~the~~ a liquid phase.

[0110] In the third aspect of the present invention, ~~said~~ the conductive particles are suspended in ~~said~~ the influent, and ~~said~~ the influent preferably further contains a strong acid ~~ion~~ ions. Preferably,

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C10 ~~said electrolysis step is followed by the a step of separating said the conductive particles and the a step of adding the separated conductive particles to said an influent again.~~

[0111] Still another aspect of the present invention provides a hydrothermal electrolytic apparatus comprising a feeder for supplying an influent containing water and reducible substances with conductive particles, and a reaction cell for subjecting ~~said the~~ influent supplied with ~~the~~ conductive particles to electrolysis at a temperature of between 100°C or more but the and a critical temperature of said the influent or less and at a pressure that allows water in ~~said the~~ influent to be kept maintained in the a liquid phase. In ~~said the~~ apparatus, ~~said the~~ reaction cell preferably has a pair of electrodes, more preferably one of which serves as an anode and the other of which serves as a cathode.

[0112] Still another aspect of the present invention provides a hydrothermal electrolytic apparatus comprising a reaction cell for supplying a direct current to an influent containing water, reducible substances and conductive particles at a temperature of between 100°C or more but the and a critical temperature of said the influent or less and at a pressure that allows water in ~~said the~~ influent to be kept maintained in the a liquid phase, and a separator for separating the conductive particles from ~~the an~~ effluent. Preferably, ~~said the~~ reaction cell has a pair of electrodes, more preferably one of which serves as an anode and the other of which serves as a cathode.

[0113] In ~~said the~~ hydrothermal electrolytic apparatus, ~~said the~~ separator preferably comprises a liquid cyclone, or the ~~Or said~~ separator preferably comprises a filter device.

[0114] In the third aspect of the present invention, the influent contains conductive particles. When a ~~dc~~ direct current voltage is applied across ~~the an~~ original cathode and ~~the an~~ original anode in a hydrothermal electrolytic apparatus supplied with ~~a an~~ influent containing conductive particles, individual conductive particles serve as an anode at ~~the~~ surfaces facing the original cathode and as a cathode at ~~the~~ surfaces facing the original anode under ~~the an~~ effect of an electric field. Therefore, a current flows locally between the original cathode and ~~the~~ surfaces of individual conductive particles serving as an anode, and also a current flows locally between the original anode and ~~the~~ surfaces of conductive particles serving as a cathode. When two conductive particles are located in proximity to but ~~without not in~~ contact with each other, and ~~the a~~ cathodic surface of one conductive particle faces ~~the an~~ anodic surface of the other conductive particle, for example, a current flows locally

between the cathodic surface and the anodic surface. This also applies to more than two discrete conductive particles, in which case a current seems to flow between ~~the a~~ cathodic surface of a conductive particle and ~~the an~~ anodic surface of another conductive particle. Therefore, ~~the a~~ surface area of electrodes can be substantially increased without increasing ~~the a~~ surface area of the original anode and the original cathode.

[0115] Preferably, conductive particles are suspended in ~~the an~~ influent. As a result, solid conductive particles can flow with the influent. This also prevents conductive particles from adhering to ~~the a~~ surface of electrodes.

[0116] Conductive particles may be wholly formed of a conductive material. Alternatively, they may be particles of a conductive material coated with another conductive material, ~~on their surfaces~~ or particles of a non-conductive material coated with a conductive material ~~on their surfaces~~. Even particles having an insulating oxide or the like deposited on their surfaces by corrosion or other reasons are regarded as conductive particles so ~~far~~ long as they are generally conductive.

[0117] Particles formed of a conductive material include, for example, carbon particles, metal particles and conductive oxide particles. Carbon particles include, for example, particles of graphite. Metal particles include, for example, so-called metal powders such as iron powder, copper powder, silver powder, nickel powder, cobalt powder and ~~aluminium~~ aluminum powder. Conductive oxide particles include particles of a ferrite and ruthenium oxide. In terms of costs, iron powder and aluminium powder are preferred. Iron powder includes powdered scrap from machining of steel (including stainless steel), cast iron or the like.

[0118] Particles of a conductive material coated with another conductive material include metal particles coated with a thin film of another metal, ~~on their surfaces~~ such as copper particles coated with platinum ~~on their surfaces~~.

[0119] Particles of a non-conductive material coated with a conductive material ~~on their surfaces~~ include particles of an oxide powder coated with a metal thin film, ~~on their surfaces~~ such as aluminum oxide particles coated with copper ~~on their surfaces~~.

[0120] Particles of a conductive or non-conductive oxide powder coated with a conductive oxide ~~on their surfaces~~ are also suitable, such as zirconium oxide particles coated with iridium oxide ~~on their surfaces~~ and silicon dioxide particles coated with ruthenium oxide ~~on their surfaces~~.

[0121] Synthetic polymer particles coated with a metal or a conductive oxide ~~on their surfaces~~ are also suitable, such as polymer particles of polyethylene glycol coated with ruthenium oxide ~~on their surfaces~~.

[0122] Means Techniques for coating a metal thin film include electroplating, electroless plating, sputtering, physical vapor deposition, chemical vapor deposition, etc and the like. Means Techniques for coating a conductive oxide thin film include calcination, sputtering, physical vapor deposition, chemical vapor deposition, etc and the like.

[0123] These conductive particles are subjected to a current in ~~the~~ a presence of a strong acid ion ions such as a halide ion ions at high temperature and high pressure. Suitable conductive particles may be irreversible particles liable to be molten or corroded under these conditions, or reusable chemically stable particles. For single use, iron powder, aluminium powder or the like are preferred in terms of costs. Reusable conductive particles preferably have such an excellent corrosion resistance that they remain insoluble even if a current is applied.

[0124] Reusable conductive particles are preferably formed of, or coated with, a conductive material having ruthenium, iridium, platinum, palladium, rhodium, copper, nickel, tin or an oxide thereof, or a ferrite.

[0125] Ruthenium, iridium, platinum, palladium, rhodium, copper, nickel and tin may be elementary metals or oxides. Alloys of these metals are also preferably used. Such alloys include, for example, platinum-iridium, ruthenium-tin and ruthenium-titanium. In some embodiments, conductive materials based on palladium, ruthenium or an alloy of platinum and iridium are especially preferred.

[0126] Conductive particles may be in any form such as, but not limited to, sphere, rod, disk, T-shape, donut, tube, fiber, etc and the like. Hollow particles are also suitable.

[0127] Conductive particles preferably have a size ~~shorter~~ less than the a distance between the an anode and the a cathode. The An average size of conductive particles is preferably 1 cm or

less, more preferably 5 mm or less, still more preferably 1 mm or less, most preferably 0.5 mm or less. For example, the a size of spherical conductive particles means their diameter. The A size of rod-like or tubular conductive particles means their length. The A size of conductive particles may be homogeneous or may widely vary.

[0128] Rod-like or tubular conductive particles preferably have an aspect ratio, ~~ie, the i.e. a~~ ratio of ~~the~~ length to ~~the~~ diameter of the rod or tube, of 0.1-1000, more preferably 0.5-100.

[0129] The An influent preferably contains at least 0.01% by weight ~~or more of~~ conductive particles, more preferably at least 0.1% by weight ~~or more of~~ conductive particles. ~~The presence~~ Pressure of conductive particles in an amount even as small as 0.01% by weight in the influent increases a current, and therefore, a voltage across ~~the~~ original electrodes.

[0130] The An influent preferably contains at most 30% by weight ~~or less of~~ conductive particles, more preferably at most 10% by weight ~~or less of~~ conductive particles. If more than 30% by weight of conductive particles are contained, ~~the~~ fluidity of the influent is affected and the a probability of a short circuit between electrodes significantly increases.

[0131] The A content of conductive particles in the an influent means ~~the~~ content in the a feed line for supplying the influent into the a reaction cell. This is because conductive particles are not always uniformly distributed in the reaction cell so that ~~the~~ content is difficult to exactly determine. When the reaction cell is tubular and ~~the~~ influent is transferred from the a bottom of the cell to the a top of the cell, for example, ~~the~~ concentration of conductive particles tends to be higher at the bottom of the reaction cell.

[0132] The third aspect of the present invention as defined above is explained in detail below with reference to Fig. 14. In Fig. 14, elements having the same operation and function as those of the treatment system shown in Fig. 13 are designated by the same reference numbers and not explained here.

[0133] In a hydrothermal electrolytic treatment system according to the third aspect of the present invention shown in Fig. 14, influent line 60 for supplying an influent is connected to reaction vessel 50. Influent line 60 preferably has a feed tank 61, a high-pressure pump 66, a heat exchanger 70 and a heater 74, and an influent can be transferred through these components in this order.

[0134] A feeder 130 for supplying conductive particles to feed tank 61 is provided. Feeder 130 comprises a hopper 132 for holding conductive particles 138, and a screw feeder 134 for quantitatively supplying conductive particles 138 to feed tank 61. A motor 136 is connected to screw feeder 134. ~~The~~ A screw of screw feeder 134 rotates with the rotation of motor 136 to introduce a metered amount of conductive particles 138 into feed tank 61. Hopper 132 may be supplied with crude conductive particles or conductive particles 112 separated by filter device 114. Feed tank 61 is equipped with a stirrer 61a for homogeneously agitating the influent.

[0135] Each ~~member component~~ on in influent line 60 has the same operation as explained ~~about~~ with regard to Fig. 13, and is not explained here.

[0136] Separately from influent line 60, an oxidizer line 80 is preferably provided. Each ~~member component~~ on in the oxidizer line also has the same operation as explained ~~about~~ with regard to Fig. 13, and is not explained here.

[0137] Preferably, reaction vessel 50 has an axially extending tubular shape, preferably a cylindrical shape. Reaction vessel 50 includes a pair of electrodes for electrolysis therein. Reaction vessel 50 has a metal inner wall 50s, which can serve as a cathode. For example, the ~~wall of~~ reaction vessel 50 may be wholly made from a metal. Reaction vessel 50 contains a rod-like anode 92 therein. Preferably, ~~the~~ an outer face of anode 92 is also cylindrical so that ~~the center~~ a central axis of anode 92 substantially coincides with ~~the center~~ a central axis of reaction vessel 50. Anode 92 may be a cylindrically shaped mesh or net, or a cylindrically shaped plate.

[0138] Positive terminal 96 and negative terminal 97 of ~~dc~~ direct current source 94 are connected to anode 92 and cathode, i.e. inner wall 50s, via lines 98, 99, respectively. Line 98 for feeding the anode passes through ~~the~~ a top 51b of reaction vessel 50, while line 98 is insulated from reaction vessel 50 by insulating member 56. When reaction vessel 50 is made from a metal, line 99 may be directly connected to reaction vessel 50.

[0139] Reaction vessel 50 may be heated by a heater ~~not shown~~ (not shown). The heater may be an electric heater, for example. ~~The outside~~ An exterior of the reaction vessel may be directly heated ~~with~~ by a burner or the like.

[0140] In the treatment system shown in Fig. 14, a recycle line 120 for recycling conductive particles is connected to the reaction vessel. Recycle line 120 comprises a separator 122 for separating conductive particles from the an effluent. Thus, conductive particles can be recycled without being discharged from the system.

[0141] Thus, ~~a~~ the separator 122 for separating solid particles from the effluent is connected to the a top of reaction vessel 50 via line 121. Separator 122 may consist of, for example, a liquid cyclone that centrifugally separates conductive particles. In the liquid cyclone, conductive particles settle at the a bottom thereof. In separator 122, all the conductive particles in the effluent may not be separated. Most of the conductive particles may be removed in separator 122, and the a remainder of the conductive particles may be removed by filter device ~~110~~ 114.

[0142] Separator 122 is connected to pump 126 via line ~~124~~ 129, and pump 126 is connected to the a bottom of reaction vessel 50 via line 127. When separator 122 consists of a liquid cyclone, a concentrated slurry containing conductive particles is obtained. This concentrated slurry can be introduced into the bottom of reaction vessel 50 by pump 126.

[0143] An effluent line 100 for discharging ~~the~~ effluent deprived of at least a part of conductive particles is connected to separator 122. Effluent line 100 preferably has heat exchangers 87/70, a gas-liquid separator 102, and ~~a~~ filter device ~~110~~ 114, and ~~the~~ effluent hydrothermally electrolyzed in reaction vessel 50 is transferred through these components in this order.

[0144] Preferably, gas-liquid separator 102 is connected to effluent line 100. Gas-liquid separator 102 separates gas and liquid in ~~the an~~ effluent. The effluent is held at a predetermined level 104 in gas-liquid separator 102. A pressure transmitter tube may be provided between ~~the a~~ space above ~~said~~ level 104 and the effluent below ~~said~~ level 104, and a level detector for determining ~~the~~ a gas-liquid interface or slurry level may be provided in this pressure transmitter tube. A level detecting mechanism ~~not shown~~ (not shown) may be designed to measure ~~the~~ level 104 by ~~the a~~ pressure difference between gas and liquid to discharge ~~the~~ effluent in such a manner that ~~said~~ level 104 may be fixed or within a fixed range. Gas-liquid separator 102 may be provided with a piezoelectric element, for converting pressure into an electric signal ~~each~~ both above and below ~~said~~ level 104, whereby this electric signal is entered into a level detector to detect the pressure difference.

[0145] Preferably, gas-liquid separator 102 has a level-controlling mechanism 106 for stabilizing ~~the~~ a level of the effluent in gas-liquid separator 102 within a fixed range. ~~Said~~ This level-controlling mechanism may have a level detector for detecting the pressure difference between gas and the effluent, a valve for discharging the effluent, and a controller for controlling the valve by a signal from the level detector. The level-controlling mechanism may have a pressure transmitter tube or a piezoelectric element.

[0146] A valve 108 is connected to gas-liquid separator 102 so that ~~the~~ treated water in gas-liquid separator 102 can be discharged into filter device 114 when valve 108 is opened. Preferably, switching of valve 108 is controlled by a signal from the level-controlling mechanism.

[0147] Gas-liquid separator 102 ~~may have a~~ has the pressure controlling mechanism for controlling ~~the~~ pressure in the gas-liquid separator within a predetermined range. ~~Said~~ The pressure controlling mechanism ~~may have~~ has, for example, a pressure detector for detecting ~~the~~ a pressure of ~~the~~ a gas phase, a valve for discharging gas, and a controller for controlling the valve by a signal from the pressure detector. The pressure-controlling mechanism preferably adjusts the pressure at a level that allows filter device 114 to accomplish smooth separation, for example. The pressure detector may have a piezoelectric element.

[0148] A valve 109 is connected to gas-liquid separator 102 so that ~~the~~ gas in gas-liquid separator 102 can be discharged to the atmosphere when valve 109 is opened. Preferably, switching of valve 109 is controlled by a signal from a pressure-controlling mechanism ~~not shown~~ (not shown).

[0149] In the embodiment shown in Fig. 14, ~~the~~ pressure of gas-liquid separator 102 and ~~the~~ pressure of reaction vessel 50 are preferably separately controlled so that the pressure of reaction vessel 50 is adjusted ~~at~~ to a pressure that allows a liquid phase to be ~~kept in~~ maintained during hydrothermal electrolysis, and the pressure of gas-liquid separator 102 is adjusted ~~at~~ to a pressure that allows dielectric particles to be smoothly filtered by filter device 114.

[0150] For example, it is especially preferred that a pressure-regulating valve 115 having a pressure sensor is separately provided ~~on~~ in line 100 to control ~~the~~ pressure of reaction vessel 50. Thus, ~~the~~ pressure of reaction vessel 50 is ~~kept~~ maintained ~~on the~~ an inlet side of valve 115, so that the pressure of reaction vessel 50 can be controlled via valve 115.

[0151] Filter device 114 filters the effluent to separate conductive particles 112 contained in the effluent. Filter device 114 may consist of a filter press, for example. ~~The effluent~~ Effluent deprived of conductive particles is stored in a container 116. On the other hand, these conductive particles 112 can be supplied to feeder 130 and recycled.

[0152] Next, a hydrothermal electrolytic process using the hydrothermal electrolytic treatment system shown in Fig. 14 is explained.

[0153] Feeder 130 supplies a desired amount of conductive particles 138 to feed tank 61 to control ~~the~~ a content of conductive particles in ~~the~~ an influent. A halide ion source is introduced from halide line 63 or the like into feed tank 61 to control its content. The influent is homogenized under agitation with stirrer 61a.

[0154] The influent in feed tank 61 is transferred by high-pressure pump 66, and the influent is preheated in heat exchanger 70 and further heated in heater 74, and then introduced into reaction vessel 50.

[0155] On the other hand, compressed air serving as an oxidizer is supplied via oxidizer line 80 ~~and~~ , preheated in heat exchanger 87, and introduced into reaction vessel 50.

[0156] After the influent and oxidizer are introduced into reaction vessel 1, electrolysis is started. Thus, ~~dc~~ direct current source 94 is turned on to supply ~~dc~~ direct current to anode 92 and reaction vessel 50 serving as a cathode. ~~The influent kept~~ Influent maintained in ~~the~~ a liquid phase under high temperature and high pressure moves from ~~the~~ a bottom to ~~the~~ a top in reaction vessel 50, during which hydrothermal reaction and electrolysis proceed at the same time to oxidatively degrade reducible substances in the influent. In ~~the~~ a presence of ~~a~~ strong acid ~~ion~~ ions and conductive particles, ~~dc~~ direct current can readily flow in the influent. ~~The~~ A heating temperature of heater 74 is appropriately lowered because heat is generated ~~with~~ from hydrothermal reaction and electrolysis.

[0157] ~~The~~ A reaction time is ~~enough~~ sufficiently long for reducible substances in the influent to be oxidatively degraded, for example 1 second to 48 hours, preferably 1 minute to 24 hours. The reaction time is more preferably 5 hours or less, still more preferably 2 hours or less. The reaction time is adjusted in ~~as~~ a function of ~~the~~ volume of reaction vessel 50 and ~~the~~ feed flow rate of the influent.

[0158] Effluent 52 is introduced into separator 122, where conductive particles in the effluent are separated. Thus, separated conductive particles are introduced with some amount of liquid into reaction vessel 50 by pump 126.

[0159] ~~The effluent~~ Effluent discharged from separator 122 is circulated through line 101, heat exchanger 87, line 102, heat exchanger 70 and valve ~~108~~ 115, and is introduced into gas-liquid separator 102.

[0160] Gas is discharged via valve 109, while liquid is introduced into filter device ~~110~~ 114 via valve ~~107~~ 108. Filter device ~~110~~ 114 further removes conductive particles to discharge the effluent into container 116

[0161] In the embodiment of the present invention shown in Fig. 14, a hydrothermal electrolytic apparatus according to the first and second embodiments of the present invention described with reference to Figs. 1-12 may be used as a hydrothermal electrolytic reactor. If a hydrothermal electrolytic apparatus having a plurality of reaction cells as shown in Figs. 1-12 is used to hydrothermally electrolyze an influent containing conductive particles, the efficiency of electrolytic reaction in hydrothermal electrolysis is further improved so that hydrothermal electrolytic treatment can be performed more efficiently. However, conductive particles contained in the an influent here should have a size smaller than ~~the~~ a distance between ~~the~~ an anode and ~~the~~ a cathode in each reaction cell.

[0162] The following examples illustrate a hydrothermal electrolytic apparatus according to the third aspect of the present invention without, however, limiting the present invention thereto.

Example 1

[0163] Experiments were made using an autoclave shown in Fig. 15. The autoclave consists of a container body 200 made from SUS304 and a cover 201, and has an inner volume of 300 ml. An exhaust port 203 is formed in cover 201 and connected to an exhaust pipe 205 having a valve 204. The container body also has a gas inlet 212 for introducing a purge gas.

[0164] A cylindrical platinum plate electrode 206 (outer diameter 26.5 mm, height 60 mm, effective area 50 cm², initial dry weight 35.525 g) was provided in the autoclave. Although electrode

206 is shown as a net member, it was not a net but a plate in this example. Electrode 206 was connected to ~~the~~ a positive electrode of outer power source 210, while cover 201 was connected to ~~the~~ a negative electrode of the outer power source so that ~~the~~ an inner wall face of the container body served as a cathode.

[0165] An artificial waste liquor consisting of 4,000 mg/L acetic acid (TOC 1,600 mg/L), 2 wt% NaCl, and tap water was prepared. Spherical particles of silicon dioxide (glass beads) were coated with copper by performing electroless plating to prepare conductive particles. These conductive particles contain 5 wt% copper on ~~the~~ a basis of ~~the~~ total weight of ~~said~~ the conductive particles. These conductive particles had an average particle diameter of 0.2 mm. To 150 mL of ~~said~~ the artificial waste liquor was added 5 g of ~~said~~ the conductive particles.

[0166] At room temperature, 150 ml of ~~said~~ the artificial waste liquor containing 5 g of conductive particles was introduced into the autoclave. Then, the autoclave was filled with argon in an amount equivalent to 3 MPa and sealed. Then, ~~the content~~ contents 220 was heated to 250°C by a heater 211 under agitation ~~with~~ via a stirring impeller 202. When ~~the~~ a temperature reached 250°C, application of a 6A constant ~~dc~~ direct current across electrodes was started and continued at 250°C for 15 minutes. During ~~then~~ this, ~~the~~ an average voltage was 7.50 V. After a lapse of 15 minutes, ~~the~~ application was stopped and the ~~content was~~ contents were cooled to room temperature. After ~~said~~ the conductive particles in ~~the~~ this influent were settled, ~~the~~ a supernatant was collected and analyzed.

[0167] This supernatant was colorless and odorless, and had a TOC of 30.4 mg/L. Thus, the TOC degradation reached 98.1%, showing ~~tat the~~ that a process of the present invention is very effective.

Comparative example 1

[0168] In this comparative example, ~~the~~ artificial waste liquor was treated under the same conditions as in the example above except that no conductive particles were added to the artificial waste liquor. When a 6A direct current was applied across electrodes, ~~the~~ an average voltage was as low as 3.04 V. After treatment, ~~the~~ an effluent showed a TOC of 954 mg/L with TOC degradation of only 40.3%.

[0169] Thus, the a current flowing in the an influent increases and the a voltage across electrodes also increases when conductive particles are suspended in the influent.

INDUSTRIAL APPLICABILITY

[0170] Hydrothermal electrolytic processes and apparatus according to various aspects of the present invention allow a large amount of waste liquor to be efficiently and continuously treated. Hydrothermal electrolytic apparatus of the present invention are well suitable for continuous processes, but also applicable to batch processes or semi-continuous processes.

ABSTRACT OF THE DISCLOSURE

~~An object of the present invention is to provide a hydrothermal electrolytic apparatus that allows a large amount of waste liquor to be efficiently treated. In order to attain this object, a~~ **A** hydrothermal electrolytic apparatus ~~according to an aspect of the present invention~~ comprises a reaction cell for electrolyzing influent at high temperature and high pressure, wherein ~~the~~ **an** overall surface area of a pair of electrodes located in the reaction cell ~~31~~ per 1 m³ of ~~the~~ volume of the influent is 0.05 m² or more. ~~A~~ **The** hydrothermal electrolytic apparatus ~~according to one embodiment of the present invention~~ has two or more tubular reaction cells each having a metal inner wall serving as a cathode, and an anode is provided in each of ~~said~~ **the** reaction cells. A hydrothermal electrolytic process ~~according to another aspect of the present invention~~ comprises incorporating conductive particles into ~~the~~ **an** influent to substantially increase ~~the~~ **a** surface area of electrodes in **during** hydrothermal electrolysis.